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# HYDROGEN PRODUCTION FROM FLUIDIZED BED STEAM REFORMING OF HYDROCARBONS

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**Abstract** – Steam reforming of methane, kerosene and heavy oil over a nickel/alumina commercial catalyst and other materials such as limestone, dolomite and iron ore, was studied using a 5 cm i.d. fluidized bed reactor. The effects of operating parameters on conversion, hydrogen yield, product gas composition and elutriation of fine catalysts were investigated. It was found that a fluidized bed is flexible enough to handle various feedstocks, including hydrocarbons heavier than naphtha, because it permits the addition of catalyst to, or withdrawals of, coked catalyst from the bed. The yield of hydrogen obtained from fluidized bed steam reforming of heavy oil at 800 °C over limestone was similar to that obtained over commercial nickel-based catalyst. This indicates that limestone could be a promising catalyst for the production of hydrogen from heavy oil. However, hydrogen yield decreased with reaction time in the experiments using the limestone catalyst. The main cause of the decrease in hydrogen yield was elutriation of fine catalysts from the bed during the reaction.

Key words: Fluidized Bed, Hydrocarbons, Steam Reforming, Hydrogen

## INTRODUCTION

Although various technologies have been developed for the production of hydrogen, steam reforming of natural gas and naphtha is predominantly employed for large scale industrial application around the world [Cornell and Helnzelmann, 1980]. Usually, nickel-based catalysts are used in steam reforming of natural gas and naphtha, and extensive studies have been made on the reaction mechanism and reaction rate of steam reforming of hydrocarbons.

$$C_nH_m + n\ H_2O \rightarrow (n+m/2)\ H_2 + n\ CO \quad (1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (2)$$

The reason why feedstock for commercial steam reforming is limited to natural gas and light naphtha is that coke is formed during steam reforming of higher hydrocarbons even at a high steam to carbon ratio [Ko et al., 1995]. When steam reforming is carried out in a fixed bed at high temperatures, normal operation is not possible as coke accumulates in the reactor. But the world-wide trend is of increasing demand of light hydrocarbons and hydrogen, while the reserve of heavy crude oil, which requires larger amounts of hydrogen in processing, is bigger than that of the light one. Thus, it is desirable to produce hydrogen from heavy oil instead of natural gas or light naphtha.

One way of realizing steam reforming of heavy hydrocarbons involves resorting to a fluidized bed which would permit continuous addition of fresh catalyst to the reactor and withdrawals of coked one from it. In the present study, a small scale fluidized bed reactor was employed for steam reforming of methane, kerosene and heavy oil, and various aspects of experimental data are discussed.

## EXPERIMENTAL

### 1. Hydrocarbons Used

Methane (99.99 % purity), kerosene (Junsei Chemical Co., extra pure) and heavy oil (Bunker-C) were tested as feedstocks for steam reforming for the production of hydrogen. In case of heavy oil steam reforming, Bunker-C is highly viscous and does not flow at room temperature. Thus heating is required to reduce viscosity prior to pumping it. But even at 50 °C its viscosity is 118-122 cp, thus still too high for adequate pumping with laboratory equipment. However, the viscosity of heavy oil drops significantly when it is mixed with kerosene. Thus 90 % Bunker-C-10 % Kerosene has significantly lower viscosity compared to 100 % heavy oil, and can be pumped without trouble at 40 °C (viscosity at this temperature is 69.2 cp). Therefore this mixture was designated as heavy oil in this study. Table 1 shows the ultimate analyses of Kerosene, Bunker-C oil and Bunker-C/Kerosene mixture used as feedstocks for steam

**Table 1. Ultimate analyses of hydrocarbons used**

| Feed stock | Kerosene | Heavy oil (90-10 % mixture) | Heavy oil (as received) |
|---|---|---|---|
| Composition (wt %) | | | |
| C | 86.0 | 82.5 | 85.9 |
| H | 14.3 | 11.8 | 12.2 |
| N | 0.2 | 0.3 | 0.3 |
| S | - | 1.3 | 1.4 |

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**Table 2. Properties of catalysts used for steam reforming of hydrocarbons**

| Catalysts | Iron ore | | Nickel based catalyst | | Limestone | | Dolomite | |
|---|---|---|---|---|---|---|---|---|
| Physical properties: | | | | | | | | |
| -size (avg. dia., mm) | 0.12 | | 0.17 | | 0.16 | | 0.16 | |
| -density (g/cm$^3$) | 4.01 | | 2.98 | | 2.80 | | 2.73 | |
| Compositions (wt %) | Fe | 62.58 | $Al_2O_3$ | 32 | Ca | 400 | CaO | 29.5 |
| | $SiO_2$ | 3.92 | CaO | 11 | Mg | 1.00 | MgO | 21 |
| | $Al_2O_3$ | 2.60 | $K_2O$ | 7 | Si | >0.02 | $Fe_2O_3$ | 0.2 |
| | S | 0.01 | MgO | 13 | Al | >0.05 | $Al_2O_3$ | 0.5 |
| | P | 0.07 | NiO | 21 | Fe | 0.04 | $SiO_2$ | 0.7 |
| | $TiO_2$ | 0.1 | $SiO_2$ | 16 | | | $SO_3$ | 0.1 |

reforming.

## 2. Catalysts Employed

Various kinds of catalysts were employed for the steam reforming such as a commercial nickel based commercial catalyst, limestone, dolomite and iron ore. In the case of nickel-based catalyst, reduction was carried out before the reforming experiment by purging the reactor with nitrogen for one hour, then flowing hydrogen while raising bed temperature to 770 °C in two hours, and then keeping a hydrogen flow of 200 cc/min for 12 hours at 770 °C. The compositions and average catalyst particle size are listed in Table 2. Catalysts were carefully sieved before being put into the reactor.

## 3. Fluidized Bed Reformer

A schematic diagram of the experimental set-up for fluidized bed steam reforming is shown in Fig. 1. Methane and nitrogen from a cylinder are fed to the reactor via a flowmeter. Distilled water fed from a burette through a metering pump vaporized in the preheating section prior to injection into the reactor. Kerosene or heavy oil, when used in place of methane as feedstock for steam reforming, was fed from a holding vessel through a metering pump into the reactor. Kerosene was vaporized in a preheating zone before being fed into the reactor while heavy oil was directly injected into the reactor to avoid coking in the feed line.

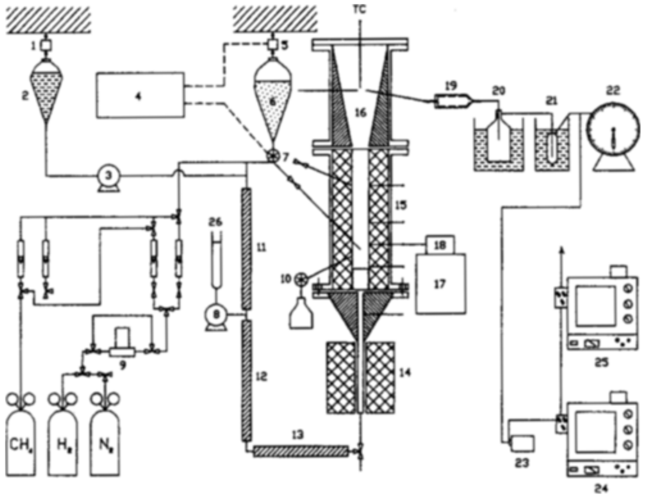

**Fig. 1. Schematic diagram of experimental set-up for fluidized bed steam reforming of hydrocarbons.**

1. Load cell
2. Water vessel
3. Metering pump
4. Controller
5. Load cell
6. Catalyst vessel
7. Rotary feeder
8. Metering pump
9. Mass flow controller
10. Rotary feeder
11, 12. Vaporizer
13, 14. Preheater
15. Fluidized bed
16. Freeboard
17. Heavy oil feeder accessories
18. High pressure metering pump
19. Dust filter
20, 21. Water trap
22. Wet gas meter
23. Master flex pump
24, 25. Gas chromatograph
26. Kerosene vessel

The reactor was constructed from a stainless steel pipe of 54.2 mm i.d. and 900 mm length. It was also equipped with a perforated type distributor with opening area of 1.57 %. To avoid bed material weeping 100 mesh stainless steel gauze was put on the distributor plate. The reactor was equipped with nozzles for the feed and withdrawal of bed material, and taps on the sidewall for the measurement of temperature and pressure inside the reactor. The reactor was heated externally with a tube-type furnace to raise the bed temperature above 800 °C.

Product gas from the reactor was kept at temperatures above 300 °C to avoid condensation of hydrocarbons and moisture in a dust catcher. After the dust catcher product gas was cooled for removal of condensables, the product gas was analyzed by two sets of gas chromatographs. $H_2$, CO, $CH_4$, $N_2$ were measured by a thermal conductivity detector with a column consisting of Molecular sieve 5A and 13X with argon as a carrier gas at 120 °C. $CO_2$, $C_2$, and $C_3$ gases were analyzed with a porapak-Q column with the helium carrier gas at 100 °C. Flow rate of product was measured by a wet gas meter.

# RESULTS AND DISCUSSION

## 1. Hydrogen Yields with Various Hydrocarbons

In Fig. 2, comparisons of hydrogen yields over a nickel-based commercial catalyst for various hydrocarbon feedstock steam reforming were carried out in a fluidized bed. Reaction temperature was 800 °C, steam to feeding carbon ratio 2.22-4.08, bed height 0.1 m and superficial gas velocity 0.2 m/s. Hydrogen production efficiency of processes can be evaluated in terms of hydrogen yield:

$$\text{hydrogen yield} = \frac{\text{moles of hydrogen produced}}{\text{moles of carbon consumed}} \quad (3)$$

The conversion of kerosene or heavy oil into gaseous products

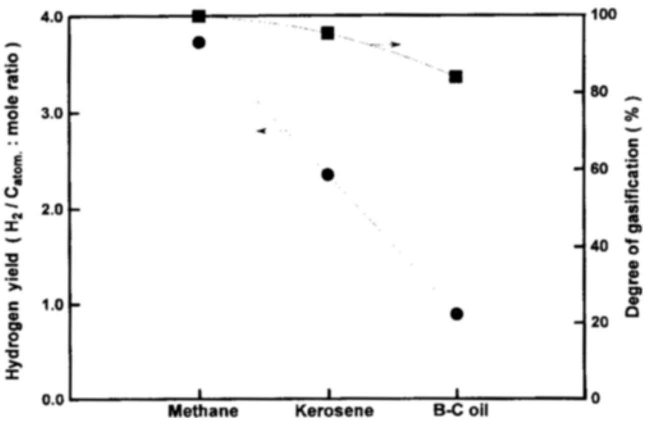

**Fig. 2. Effects of hydrocarbon rank on hydrogen yield and gasification. Reaction conditions: temperature 800 °C, steam/$C_{atom}$ 2.22-4.08, bed height 0.1 m, gas velocity 0.2 m/sec, catalyst ICI 46-1.**

was not complete and a part of outlet stream from the reactor condensed when cooled. Therefore, the degree of gasification as a measure of gasification of liquid feedstock in the reactor was defined as follows:

$$\text{degree of gasification (\%)} = \frac{\text{total mole of carbon in gaseous products}}{\text{total mole of carbon in the feed}} \tag{4}$$

As can be seen in the figure, feedstocks with higher hydrogen to carbon ratio, such as methane, give higher hydrogen yield. Hydrogen yield was sharply decreased with lower hydrogen to carbon ratio. When the water shift reaction is complete, the maximum hydrogen yield from stoichiometry can be given as 2+0.5 m/n by Eqs. (1), (2). Thus it was observed that feedstock with high hydrogen to carbon ratio gives higher yield in practice. The degree of gasification, as shown in Fig. 2, was slightly decreased with lower hydrogen to carbon ratio. It was not feasible to measure quantity of condensed liquid products that might be a product of pyrolysis. No attempt was made to analyze their composition, as the primary object of this study is the production of hydrogen.

## 2. Hydrogen Generation Ratio for Various Catalysts

Steam reforming of methane is a well-established reaction for the manufacture of hydrogen [Rostrup-Nielsen, 1984]. However, in the case of other hydrocarbons, especially for heavy oils, a quantitative investigation of the reaction scheme for hydrogen is very difficult because the hydrocarbons consist of complex components and many side reactions are involved during the reforming reaction.

The only reactions by which hydrogen can be produced in significant quantities may be expressed by the equations

$$CH_x + H_2O \rightarrow CO + \left(1 + \frac{x}{2}\right) H_2 \tag{5}$$

$$CH_x + 2H_2O \rightarrow CO_2 + \left(2 + \frac{x}{2}\right) H_2 \tag{6}$$

The maximum hydrogen yield possible by steam reforming is therefore

$$(H_2)\text{calc.} = \left(1 + \frac{x}{2}\right) CO + \left(2 + \frac{x}{x}\right) CO_2 \tag{7}$$

The values calculated by (7) are sensitive to errors in the analysis of carbon monoxide and carbon dioxide in the exit gas. The ratio of hydrogen yield obtained by experiment, $(H_2)$exp., to the maximum value given by (7) is defined as the hydrogen generation ratio.

$$\text{Hydrogen generation ratio (HGR)} = (H_2)\text{exp.}/(H_2)\text{calc.} \tag{8}$$

The values of HGR can be explained in terms of reaction characteristics.

(i) When HGR exceeds 1.0, hydrogen generation is mainly by cracking of hydrocarbons.

(ii) When HGR is close to 1.0, the reforming is dominant for hydrogen generation.

(iii) When HGR is smaller than 1.0, hydrogen, carbon dioxide or carbon monoxide are generated by other reactions instead of steam reforming.

Bunker-C oil was reformed with steam over nickel-based commercial catalyst, limestone, dolomite and iron ore catalysts under various reaction conditions in a fluidized bed. Fig. 3 shows a comparison of the HGR values over the various catalysts. High values of HGR indicate that cracking of Bunker-C was dominant for the iron ore. On the other hand, the HGR values of the nickel-based commercial catalyst, limestone, dolomite are in the range of 0.8 to 1.2. Notice that nickel-based catalyst can be easily poisoned by sulfur compounds, so its reactivity cannot be high any way for heavy oil with more than 1 % sulfur. Sand was used as a reference material, and cracking was dominant instead of reforming in this case. Therefore, it can be concluded that limestone and dolomite function as reforming catalyst as good as nickel-based catalyst on heavy oil steam reforming, while iron ore is suitable for cracking of hydrocarbons. The degree of gasification and product compositions are shown in Fig. 4. The hydrogen concentrations of pro-

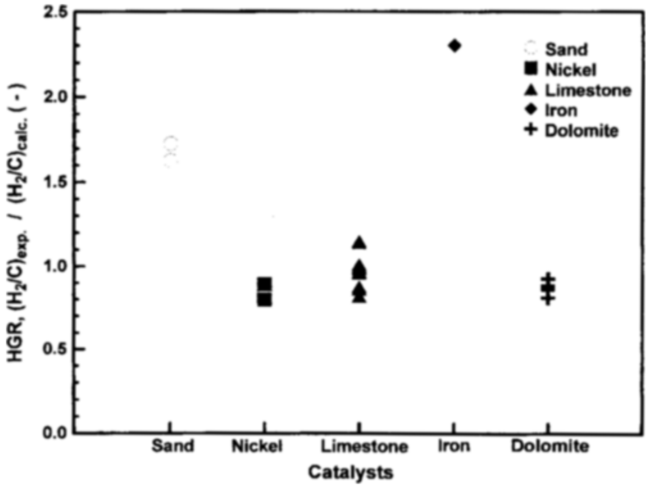

**Fig. 3. Comparison of hydrogen generation ratio of various kinds of catalysts. Hydrocarbon feed stock Bunker-C, temperature 800 °C, steam/$C_{atom}$ 1.29-11.856, bed height 0.1 m, superficial gas velocity 0.2 m/sec.**

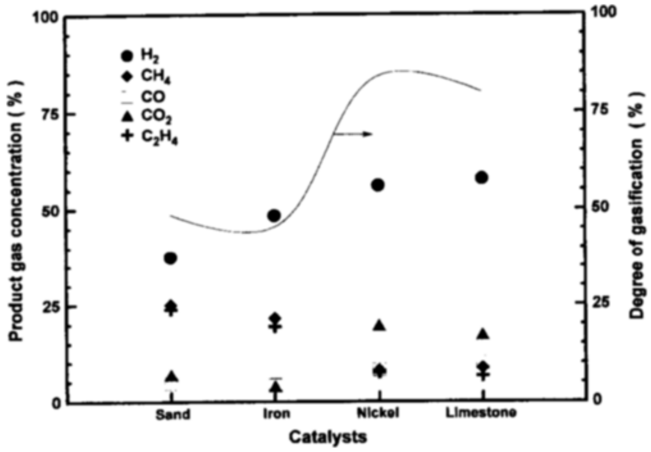

**Fig. 4. Comparison of average product gas concentration and gasification for various kinds of catalysts. Reaction conditions as in Fig. 3.**

duct gas over nickel-based commercial catalyst and limestone were higher than that of the iron ore. The degrees of gasification for nickel-based commercial catalyst and limestone showed higher values than that of iron ore.

In Table 3, hydrogen yields for various catalysts are summarized. As shown in the table, limestone particles gave higher hydrogen yields. For steam reforming of heavy oil, therefore, limestone was found to be more effective compared with nickel-based commercial catalyst. No specific component of catalysts employed in this study shown in Table 2 could be well matched with catalytic activity. Further work is needed to find the relationship between properties of catalysts and their catalytic activity. Steam to carbon ratio affected neither degree of gasification nor hydrogen yield within the experimental ranges.

### 3. Effects of Fluidized Bed Temperature

The effect of temperature on hydrogen yield and degree of gasification, methane conversion (methane reforming) is shown in Fig. 5. It should be noted that these data for methane and Kerosene were obtained with a nickel-based commercial catalyst, while those for heavy oil were with limestone at a temperature range from 700 to 800 °C. Although the hydrogen yield differs significantly among different feedstocks, the effect of temperature was moderate. Methane conversion was low at 25-29 %, and the degree of gasification of kerosene and heavy oil increased with temperature. The results from temperature variation suggest that methane reforming in a fluidized bed is not effective due to limited contact time between the reactant gases and the catalyst. However, an increase in the degree of gasification for kerosene and heavy oil with temperature leads to higher hydrogen yields.

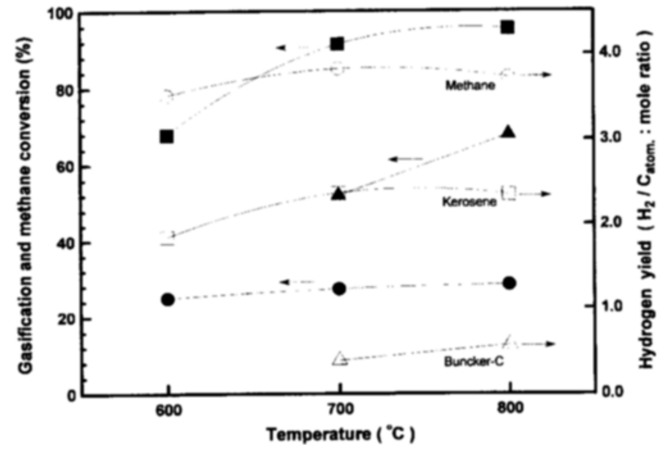

**Fig. 5. Effect of temperature on hydrogen yields and gasification for various hydrocarbons in the fluidized bed reactor. Methane and kerosene reforming: catalyst ICI 46-1, steam/C atom 3.57-4.21. Heavy oil reforming: catalyst limestone, steam/C$_{atom}$ 2.37-2.85, bed height 0.1 m, superficial gas velocity 0.2 m/sec.**

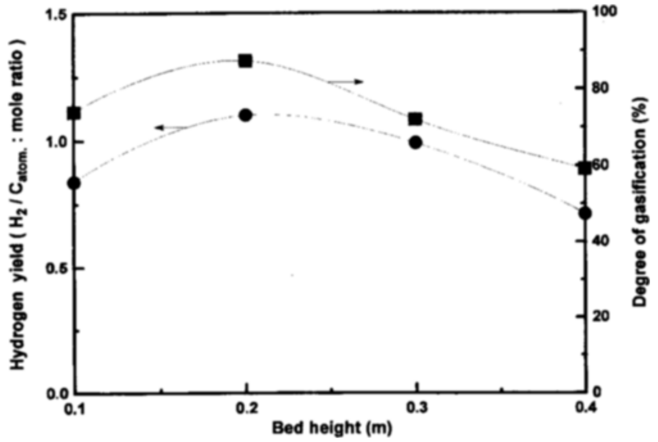

**Fig. 6. Effect of bed height on hydrogen yields for Bunker-C oil steam reforming over limestone catalyst. Temperature 800 °C, steam/C$_{atom}$ 3.70-4.34, superficial gas velocity 0.2 m/sec.**

### 4. Effect of Bed Height

As shown in Fig. 6, the degree of gasification and hydrogen yield increased with bed height, because the increase in catalyst loading helped to enhance the contact time between the reactant gas and the catalyst. However, a further increase in bed height deteriorates fluidized bed performance due to the onset of slugging. The slugging usually formed by coalescence with bubbles at a high ratio of bed depth to bed diameter

**Table 3. Hydrogen yield of steam reforming of heavy oil using different catalysts**

| Catalysts | Sand | Iron ore | Nickel based catalyst | Limestone | Dolomite |
|---|---|---|---|---|---|
| Hydrogen yield | | | | | |
| $H_2/C_{atom}$, mole ratio | 0.198 | 0.29 | 0.89 | 0.93 | 0.76 |
| kg $H_2$/kg feedstock, mass ratio | 0.0272 | 0.0398 | 0.1223 | 0.1404 | 0.1045 |

Reaction conditions: bed temperature 800 °C; bed height 0.1 m; fluidizing velocity 0.2 m/sec; $H_2O/C_{atom}$ 1.55-1.66.

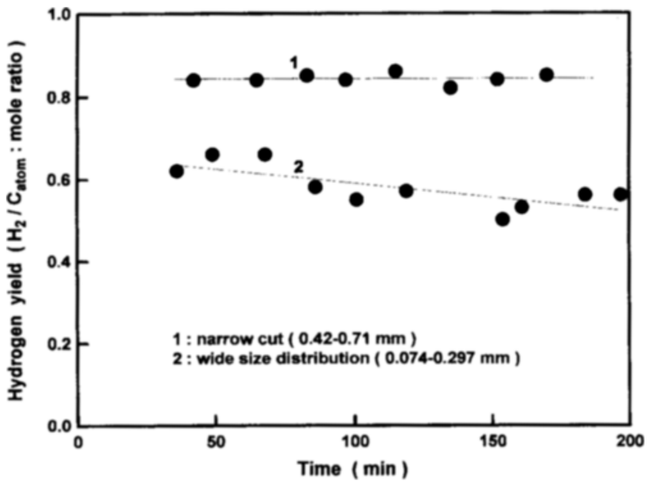

**Fig. 7. Effect of particle size distribution of limestone catalyst on hydrogen yield of Bunker-C steam reforming with reaction time. Temperature 800 °C, steam/$C_{atom}$ 2.37-2.41, bed height 0.1 m, superficial gas velocity 0.2 m/sec.**

[Kunii and Levenspiel, 1969]. The temperature distribution along the bed height indicated slugging in the bed. Due to a rough particle surface, limestone induced slugging more often compared to nickel catalyst.

### 5. Elutriation Effect

One of the most important issues in the application of a fluidized bed is attrition of bed material as excessive attrition may lead to the unbearable loss of material and difficulties with operation by fine particles entrained downstream. If catalyst particles are not reasonably attrition-resistant, their size distribution will change and attrited fine particles will be elutriated from the reactor. Then this loss of catalyst should be made up continuously for proper operation of the fluidized bed reactor.

To investigate the influence of elutriation, two limestone catalysts which have different particle size distribution were employed. One had a narrow cut distribution from 0.42 to 0.71 mm, while the other a wide size distribution containing fine particles from 0.297 to 0.074 mm. Fig. 7 shows the hydrogen yield change with time for two samples of different particle size distribution. As shown in the figure, the hydrogen yield of the narrow cut sample did not change during the reaction with time. However, the deterioration of hydrogen yield was observed for the sample containing fine particles due to elutriation of the catalyst.

## CONCLUSIONS

Bunker-C oil, kerosene and methane were reformed with steam over nickel-based commercial catalyst, limestone, dolomite, iron ore catalyst under various conditions in a fluidized bed; and hydrogen yield, degree of gasification, product gas compositions, and reactor performance were investigated. The fluidized bed showed flexibility with feedstock such as hydrocarbon heavier than naphtha because it permits the addition of catalyst to, and withdrawals of, coked catalyst from the bed. The hydrogen yield obtained from fluidized bed steam reforming of Bunker-C oil at 800 °C over limestone was similar to that obtained over commercial nickel-based catalyst. This indicates that limestone could be a promising catalyst for the production of hydrogen from heavy oil by fluidized bed steam reforming although more work is needed.

## REFERENCES

Cornell, G. and Helnzelmann, F. J., "Hydrogen for Future Refining," *Hydrocarbon Processing*, Aug., 85 (1980).

Ko, K.-D., Lee, J. K., Park, D. and Shin, S. H. "Kinetics of Steam Reforming over Ni/Alumina Catalysts," *Korean J. Chem. Eng.,* **12**, 478 (1995).

Kunii, D. and Levenspiel, O., "Fluidization Engineering," John Wiley & Sons, Ind., New York (1969).

Rostrup-Nielsen, J. R., in "Catalysis Science and Technology" (Anderson, J. R. and Boudart, M., Eds.), Springer-Verlag, Berlin, Vol. 5, chaper 1 (1984).